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FUEL RETENTION IMPROVEMENT
AT HIGH TEMPERATURES IN
TUNGSTEN-URANIUM DIOXIDE
DISPERSION FUEL ELEMENTS
BY PLASMA-SPRAY CLADDING

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SUMMARY

An investigation was undertaken to determine the feasibility of depositing integrally bonded plasma-sprayed tungsten coatings onto 80-volume-percent tungsten - 20-volume-percent uranium dioxide composites. These composites were face clad with thin tungsten foil to inhibit uranium dioxide loss at elevated temperatures, but loss at the unclad edges was still significant.

By preheating the composite substrates to approximately 3700° F in a nitrogen environment, metallurgically bonded tungsten coatings could be obtained directly by plasma spraying. Furthermore, even though these coatings were thin and somewhat porous, they greatly inhibited the loss of uranium dioxide. For example, a specimen that was face clad but had no edge cladding lost 5.8 percent uranium dioxide after 2 hours at 4750° F in flowing hydrogen. A similar specimen with plasma-spray-coated edges, however, lost only 0.75 percent uranium dioxide under the same testing conditions.

INTRODUCTION

A homogeneous dispersion of uranium dioxide in a tungsten matrix is under investigation as a potential fuel material for nuclear rocket reactors (refs. 1 and 2). Unfortunately, at the high operation temperatures of interest for this application (greater than 4000° F), uranium dioxide (UO₂) has a high vapor pressure. Consequently, exposed UO₂ is rapidly lost from the fuel composites at elevated temperatures. In a previous study (ref. 3), a thin cladding of unalloyed tungsten on the surfaces of fuel plates greatly reduced the rate of UO₂ loss. The top and bottom surfaces of such fuel plates (approx. 1- by 6- by 0.030-in.) were clad with 0.001 to 0.003 inch of tungsten either by a powder-metallurgy technique or by hot rolling tungsten foil onto the surfaces (refs. 2 and 3). Such techniques, however, did not readily provide a way to clad the plate edges. For this reason and also in order to develop methods of cladding

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specimens of more complex geometry, alternative cladding methods are being explored. The investigation reported herein was undertaken to determine the feasibility of depositing integrally bonded plasma-arc-sprayed tungsten (W) coatings onto 80-volume-percent W - 20-volume-percent UO₂ substrates and to evaluate the effectiveness of the resultant coatings in inhibiting UO₂ loss at high temperatures.

EXPERIMENTAL PROCEDURE

Materials

The specimens to be plasma sprayed were portions of rolled sheet composites (80-percent W and 20-percent UO₂) in which the UO₂ was dispersed originally in the form of 30- to 60-micron average-particle-diameter microspheres. Fabrication of such fuel sheet is described in reference 1. All specimens were electrodischarge machined into $\frac{3}{4}$ - by $1\frac{1}{4}$ -inch rectangles from larger plates that had been face clad by the roll-cladding technique described in references 1 and 2. The density of these clad composites was greater than 98 percent of the theoretical density. All specimen edges were lightly dressed with 300-grit silicon carbide paper and ultrasonically cleaned in acetone. This procedure removed surface contamination without removing the surface UO₂ particles. Finally, the specimens were washed in chemically pure acetone, air dried, and stored in a desiccator until they were used in the spraying operation.

The spray powder was a commercial -70- to 44-micron grade of tungsten that is commonly used in plasma spraying.

Plasma Coating

Preliminary investigations were made by using standard spray procedures in a water-cooled environmental chamber. These initial trials were carried out in high-purity argon (99.95-percent argon), and spraying was carried out on roughened substrate surfaces. The specimens were cooled during the spray deposition with high-purity argon. The poor bond quality of the resultant deposits indicated that these standard plasma-spray techniques were not satisfactory.

A subsequent investigation by one of the authors (ref. 4) indicated that if polished worked-tungsten substrates were preheated to 2000° to 2700° F before plasma spraying, a true metallurgical bond was established at the instant of impact between the hot tungsten particles and the substrate. This bonding suggested that the procedure could be extended to the W-UO₂ composites. This belief was substantiated by additional exploratory studies made on W-UO₂ substrates in which the effect of torch-to-substrate distance on the coating-substrate bond was examined.

All plasma spraying in the present investigation was accomplished by using the same spray equipment described in reference 4. After loading a specimen into the environmental chamber, evacuating the chamber to 20 microns, and back filling to 1 atmosphere with high-purity dry nitrogen, the torch was oper-

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ated at these fixed conditions:

Diameter of nozzle, in.	7/32
Current, amp	400
Voltage, v	60
Plasma gas, standard cu ft/hr:	
High-purity dry nitrogen	80
Commercially pure hydrogen	10
Carrier gas, high-purity dry nitrogen, standard cu ft/hr	10
Auger-type powder-hopper setting, units	11.9

Each specimen edge of the face-clad composite specimens was preheated with the effluent plasma until it reached the desired temperature, and that edge was then sprayed. This preheating and spraying sequence was repeated for each of the four edges coated. After being sprayed, each specimen was permitted to cool to room temperature in the nitrogen environment before it was removed from the chamber.

For the W-UO₂ specimens employed in this investigation, the maximum torch-to-substrate distance (thus, the minimum substrate temperature) at which some metallurgical bonding could be obtained was 3 inches. At this distance, which corresponds to a substrate temperature of about 3000° F, complete interfacial bonding did not occur. Spraying the composites at a higher substrate temperature, but below that at which much of the UO₂ would be lost by evaporation, therefore appeared to be desirable to ensure more complete and uniform metallurgical bonding. Since the substrate temperature rises quite rapidly at shorter working distances (ref. 5), a torch-to-substrate distance of 2 inches was used in the final studies. This distance was selected from the exploratory studies previously mentioned and corresponds to a substrate temperature estimated to be about 3700° F. Even though working distances of less than 2 inches might result in coatings of higher as-sprayed densities, shorter distances were not used since the resultant substrate temperatures would be sufficient to promote rapid volatilization of UO₂.

In this study, the thickness of the sprayed-tungsten cladding was made a variable for the purpose of evaluating the UO₂ retention at high temperatures. Cladding thickness was varied from 0.003 to 0.018 inch by controlling the number of passes made with the hand-operated spray torch across a given preheated edge. A layer about 0.0006 inch thick was deposited at each pass.

Evaluation of Uranium Dioxide Retention

In order to evaluate the effectiveness of the plasma-sprayed claddings in retaining the UO₂ at high temperatures, specimens were heated for 2 hours in flowing hydrogen (34 cu ft/hr measured at standard conditions, hereinafter referred to as standard cu ft/hr) at one of two temperature levels, 4500° or 4750° F. The loss in weight of the specimen as a result of this thermal treatment was used as a measure of the UO₂ loss.

Prior to the 4500° or the 4750° F tests, the as-sprayed specimens were

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annealed in hydrogen for 1/2 hour at 3000° F. The purpose of this treatment was not only to relieve any stresses in the specimen and the coating but also to remove any surface oxides before the pretest weight of the specimen was measured. The subsequent high-temperature tests were conducted in a zirconia-lined induction furnace, which is described in the appendix.

Uranium dioxide losses were obtained by weighing a specimen to the nearest 0.1 milligram both before and after the high-temperature treatment. The resultant weight loss was assumed to be entirely due to volatilization of UO_2 . This loss in weight of the specimens was corrected for small amounts of tungsten pickup that occurred during the 4750° F tests as a result of tungsten transport from the susceptor. The correction was obtained by heating a pure tungsten calibration block along with the test specimens. (Tungsten pickup by the block was never greater than 0.0003 g.) The tungsten calibration block also contained a blackbody hole that permitted accurate temperature measurements ($\pm 40^\circ$ F) with a micropyrometer.

Supplemental metallographic examinations were made on etched and unetched sections. Microstructures both parallel to (longitudinal section) and perpendicular to (transverse section) the face cladding did not differ except for the shapes of the UO_2 particles, which were somewhat elongated in the rolling direction.

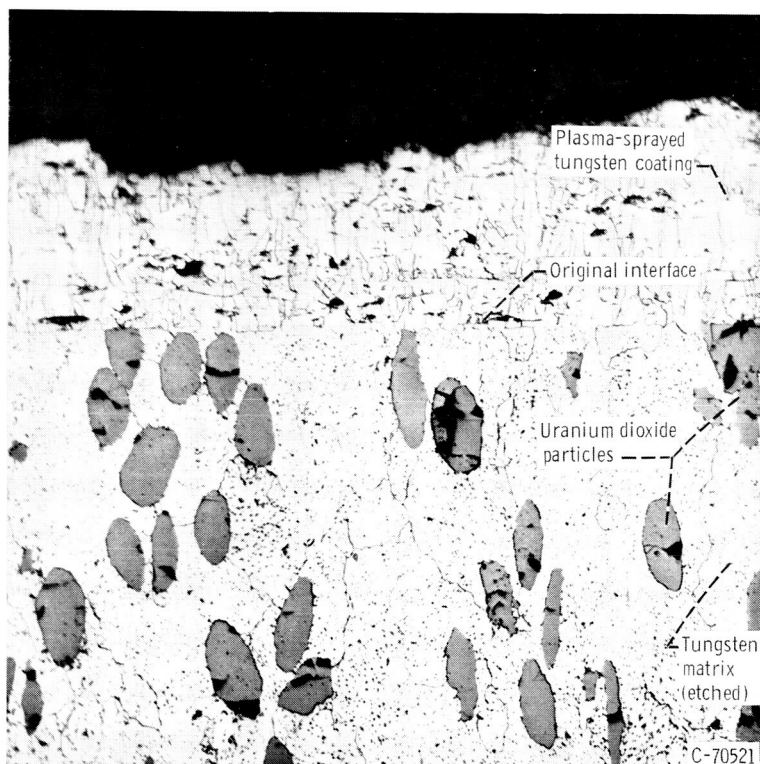


Figure 1. - Transverse cross section of tungsten coating on tungsten - 20-volume-percent uranium dioxide substrate as sprayed at torch-to-substrate distance of 2 inches (substrate preheat temperature of approx. 3700° F). Etchant, Murakami's reagent. X250.

RESULTS AND DISCUSSION

A typical transverse cross section of a W- UO_2 composite plasma spray clad on the edges is shown in figure 1. The initial large grain size of the tungsten substrate, with subsequently fewer surface grain boundaries, apparently inhibited a complete continuity of coating-substrate grain boundaries. This is in contrast to the degree of continuity previously observed in the case of tungsten sprayed onto worked commercial tungsten plate (ref. 4). The typical columnar structure of the coating can be seen, however, and the bond appears to be of high quality. Subsequent heating in hydrogen for 1/2 hour at 3000° F (the bakeout treatment) had no

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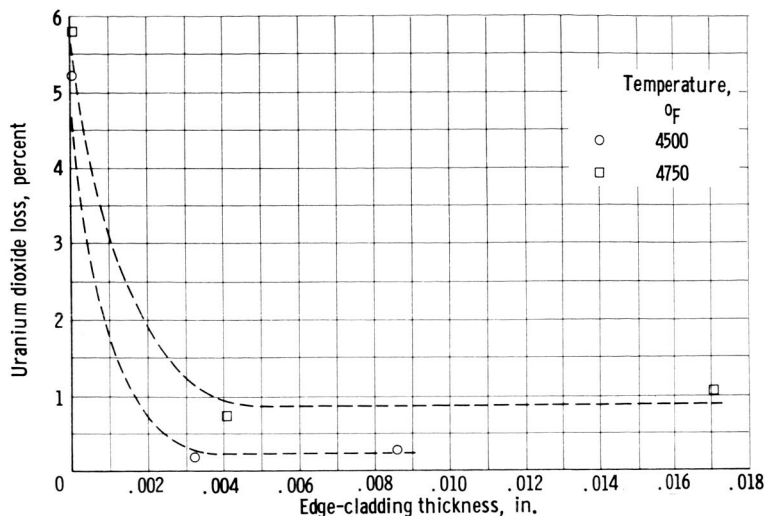


Figure 2. - Effect of plasma-sprayed-coating thickness on uranium dioxide loss from 80-percent tungsten - 20-percent uranium dioxide composites. Specimen size, 0.75 by 1.25 by 0.040 inch; roll-clad faces; all edges plasma-spray clad; time at temperature in flowing hydrogen, 2 hours.

effect on the as-sprayed microstructure, and coating recrystallization was not observed until the specimens were heated to 3500° F for 1/2 hour.

The results of the weight-loss studies at 4500° and at 4750° F can be seen in figure 2. This figure is a plot of the percentage of UO_2 loss against the edge cladding thickness for the specimens examined in this study. The specimens with no edge cladding are represented by the weight-loss data at the zero thickness value. In this plasma-spray study a minimum thickness of approximately 0.003 to 0.004 inch of cladding was required to ensure complete substrate coverage because of the lack of uniform traverse rates caused by hand operation of the torch. Even at the lowest complete plasma-coating thickness obtained, very prominent reduction in the loss of UO_2 was achieved (see fig. 2). At 4750° F, for 2 hours in flowing hydrogen, for example, UO_2 loss was decreased from 5.8 percent at zero cladding thickness to 0.75 percent loss with 0.004 inch of cladding.

The effectiveness of thin plasma-sprayed claddings in inhibiting UO_2 loss from the tungsten matrix is further demonstrated in figures 3 and 4, which show similar cross sections of the specimen with no edge cladding and with 0.004 inch of edge cladding, respec-

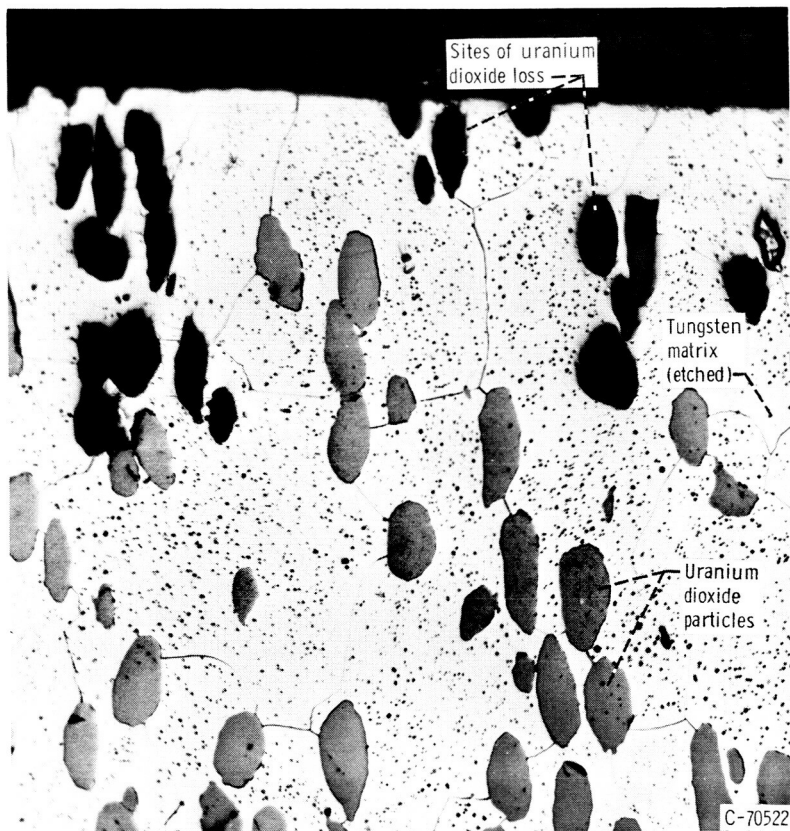


Figure 3. - Transverse cross section of uncoated tungsten - 20-volume-percent uranium dioxide specimen after heating for 2 hours in flowing hydrogen at 4750° F. Etchant, Murakami's reagent. X250.

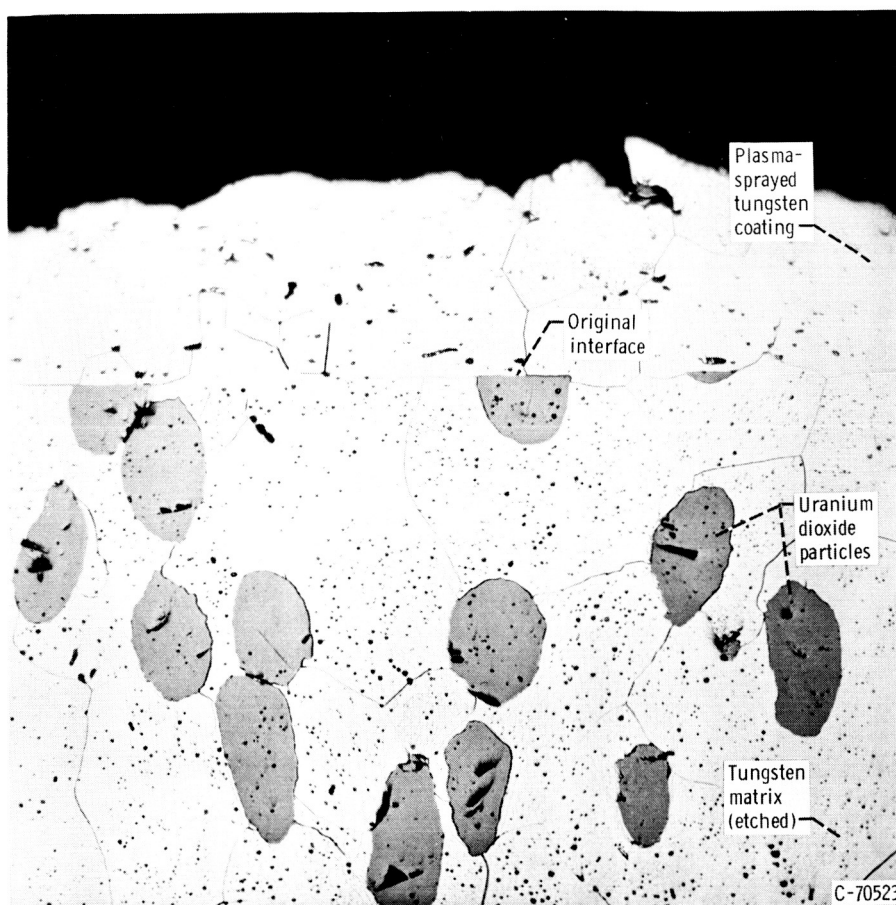



Figure 4. - Longitudinal cross section of tungsten-plasma-spray-coated tungsten - 20-volume-percent uranium dioxide specimen after heating for 2 hours in flowing hydrogen at 4750° F. Etchant, Murakami's reagent. X250.

tively. The former exhibits a marked loss of UO_2 , while no visible loss of UO_2 can be observed in the latter, even though there is some porosity visible in the coating. This observation is especially noteworthy since several of the fuel particles shown in figure 4 were apparently sectioned prior to spraying, and the cladding effectively contained them. Similar results were observed upon examination of the specimens tested at 4500° F.

Comparison of the microstructures shown in figures 1 and 4 indicates that the sprayed coating underwent recrystallization and grain growth during testing for 2 hours in hydrogen at 4750° F. Some decrease in coating porosity apparently occurred during this sequence.

This study demonstrated that plasma-sprayed coatings, deposited by the techniques of reference 4, successfully retained UO_2 in the W- UO_2 composites when tested at 4750° F for 2 hours in hydrogen. This spray coating technique may thus be able to contribute to certain aspects of materials fabrication required for high-temperature nuclear reactors.



CONCLUSIONS

From an investigation to determine the feasibility of depositing integrally bonded plasma-sprayed tungsten coatings onto 80-volume-percent tungsten-20-volume-percent uranium dioxide composites the following conclusions were drawn:

1. Good-quality metallurgically bonded tungsten coatings can be achieved by plasma spraying tungsten onto the edge of uranium dioxide composites when the substrate is preheated to approximately 3700° F in a nitrogen atmosphere before the plasma spraying.

2. Such edge coatings are very effective in reducing the uranium dioxide loss from the edges of face-clad specimens during subsequent elevated temperature testing. The uranium dioxide loss from an 80-percent-tungsten - 20-percent uranium dioxide specimen tested at 4750° F for 2 hours in flowing hydrogen, for example, was reduced from 5.8 percent for a specimen with no edge cladding to 0.75 percent for a specimen with a 0.004-inch-sprayed-tungsten coating on the edges. This low loss of uranium dioxide was experienced in spite of the presence of some porosity in the coating.

Lewis Research Center

National Aeronautics and Space Administration

Cleveland, Ohio, July 27, 1964

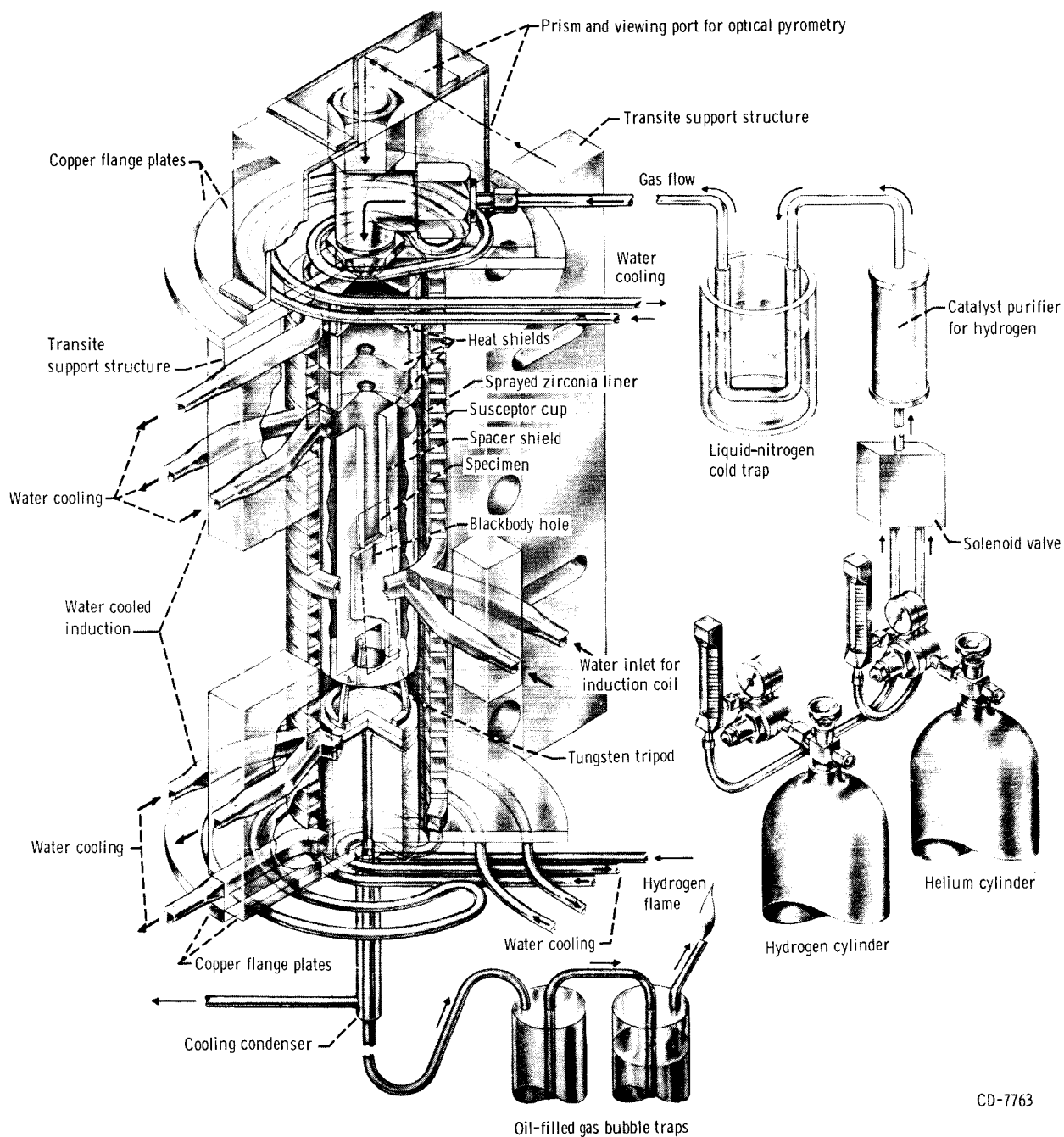


APPENDIX - HYDROGEN-ATMOSPHERE INDUCTION FURNACE

The furnace used for evaluating the loss of UO_2 from W- UO_2 compacts at high temperatures is shown in figure 5. The furnace was designed and built by NASA personnel and is powered by a 75-kilovolt-ampere motor generator that operates at a frequency of 10,000 cps. The upper temperature capability is about 5000° F for a furnace life beyond 100 hours, when a tungsten susceptor cup (2-in. O.D.; 6-in. length; 0.050-in. wall) and a hydrogen flow rate of 10 to 40 standard cubic feet per hour is used.

Details of construction not apparent in figure 5 include the following: The turns of square copper tubing are spaced 1/16 inch apart and are held by brass pins that are brazed to the outside diameter of each turn and are inserted into properly spaced holes in the Transite support structure. The space between the turns is filled with castable zirconia. The outside of the turns is insulated with a thin layer of castable zirconia and a layer of alumina about 3/4 inch thick and sealed with fiber glass impregnated with an epoxy resin.

The entire inner surfaces of the turns are sprayed with zirconia by a rod-flame spray apparatus. Entry to the furnace is possible from either top or bottom, but normally top entry only is used for access to the susceptor cup, specimen loading, etc.



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Figure 5. - Hydrogen atmosphere induction furnace used in fuel-loss tests.



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